

Transport of Optically Active Particles from the Surface Mixed Layer

William M. Balch

Bigelow Laboratory for Ocean Sciences, POB 475, W. Boothbay Harbor, ME 04575
phone: (207) 633-9600 fax: (207) 633-9641 email: bbalch@bigelow.org

Cynthia H. Pilskaln

Bigelow Laboratory for Ocean Sciences, POB 475, W. Boothbay Harbor, ME 04575
phone: (207) 633-9600 fax: (207) 633-9641 email: cpilskaln@bigelow.org

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<http://www.bigelow.org>

LONG-TERM GOALS

To determine the mass balance of optically-active particles within the surface boundary layer and to identify processes responsible for their redistribution.

OBJECTIVES

- 1) Perform manipulative experiments in which known quantities of optically-active CaCO_3 particles are introduced into the surface mixed layer then tracked over time and space. This approach effectively removes uncertainty in the production term of the mass balance equation.
- 2) Quantify the relevant physical and biological loss terms that remove optically-active particles from the mixed layer (vertical mixing, sinking of discrete particles, particle aggregation, dissolution, and grazing-related repackaging of particles into fecal pellets).

APPROACH

The focus of the Chalk-Ex project has been multidisciplinary field experiments wherein patches of optically active particles were created within the mixed layer by dispersal of Cretaceous chalk (CaCO_3) from the stern of a research ship. Patch evolution was determined from repeated spatial surveys of optics and physical properties over periods of 2-4 days. Associated with the chalk deployments and optical surveys (Balch), were Lagrangian and hydrographic drifter deployments (Plueddemann, WHOI; Fig. 1), drifting sediment trap deployments, determination of particulate export (Pilskaln; Fig. 1) and measurements of grazing and aggregation from in-situ samples (Dam/McManus; Univ. Conn.).

WORK COMPLETED

During this project, we completed 2 two-week cruises aboard the R/V Endeavor (one during November 2001 and the second during June 2003). Each cruise involved the production of two, 13T patches of Cretaceous chalk of approximately 2 square km area, deployment of drogues and drifting sediment traps within the patches, followed by surveys of the optical, physical, biological properties through time. One patch per cruise was made within the Gulf of Maine in the middle of the Jordan

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Basin (hereinafter referred to as the “north site”) while the other was several hundred miles SE of Cape Cod, over the Continental Slope (the “south site”). Significant data processing work followed each cruise. The Chalk-Ex group convened PI meetings semiannually over the course of the project at the University of New Hampshire, to plan cruises, review results and plan presentations and papers.

Optical measurements (Balch)- Surface underway optical measurements of attenuation, absorption, scattering and backscattering were made during wagon-wheel and radiator surveys of the chalk patches described above. Water-leaving radiance and downwelling irradiance (for calculating remote sensing reflectance) were measured from the bow of the R/V Endeavor using a Satlantic SeaWiFS Aircraft Simulator (SAS). A towed, undulating Scan-Fish with Wet-Labs ECO-VSF attached, allowed real-time mapping of the patch. Free-fall vertical profiles of spectral downwelling and upwelling radiance were made using a Satlantic radiance profiler that allowed high-resolution estimation of diffuse attenuation coefficients. For vertical profile stations, discrete water samples were taken with a rosette sampler, at 6-8 depths within and below the mixed layer. Subsamples were filtered for suspended CaCO_3 analyses (Fernández et al. 1993), using inductively-coupled plasma atomic absorption (ICPAA). The total and acid-labile backscattering of these samples also was measured. The loss of backscattering following seawater acidification (to a pH of 5.8), was well-correlated to the suspended calcite which allowed us to quickly verify the chalk concentrations in real-time. A tethered surveillance balloon, with video recorder suspended beneath, was launched after chalk deployment in order to determine the aerial distribution and physical attributes of the chalk patch. The balloon was typically elevated to ~190m above the ship, trailing ~360m aft. Composite images of the patches were assembled for analysis of the chalk distributions. Patch deployment was timed for clear sky conditions in order to facilitate NASA satellite ocean color observations.

We processed hundreds of discrete samples from each patch deployment. These discrete ICPAA samples of suspended calcite allowed the final checks on the calibration between backscattering and chalk concentration. Moreover, they provided periodic absolute checks of the PIC concentration in the patches. We recently performed a synthesis of the complete data set (both fall '01 and summer '03 cruises), showing Lagrangian-corrected maps of the chalk, based on Scanfish optical/CTD results integrated throughout the surface waters. A major part of our data analysis involved perfecting Krigging techniques for optimal contouring of the data and visualizing the patch dispersion. Krigging methods involve analysis of the covariance matrix along the cruise track, then applying these covariance estimates when contouring between sample lines. These Krigging techniques have proved best for contouring geochemical data in space and time. They also allow determination of statistical errors of the contouring.

Sediment Trap Program and Particle Fluxes (Pilskaln)- In order to quantify the vertical export below the patch of Cretaceous chalk (due to biological and/or physical aggregation of the chalk particles), VERTEX-style MultiPIT drifting sediment traps (Knauer et al. 1979; Knap 1993) were deployed just below the base of the mixed layer within and outside each patch. MultiPIT trap "crosses" consisting of 8 collection tubes, were attached to a drifter mooring inside each patch. During the November cruise, we deployed a drifting sediment trap array outside the patch. This had one MultiPIT trap cross located at the same depth as the trap cross within the patch. Following the deployment of the un-instrumented surface drifter into the patch and a rough determination of the surface drift, we deployed the inside-patch trap array and tracked it for 2 days. Of the trap crosses on each array, four trap tubes were designated for stable isotope analyses. Cretaceous chalk has a unique $\delta^{18}\text{O}$ signature relative to modern planktonic carbonates that makes it easy to trace in the water column and it provided the

means to verify that collected material in the traps originated from the patch. The second set of four trap tubes per drifting array (inside and outside the patches) were designated for microscopic and geochemical analyses. During the June '03 cruise, we deployed both traps within each patch, due to the fact that the outside patch drifter could not be considered an absolute control (due to spatial differences). Moreover, it allowed us to double the amount of material collected, and provided replication within the patch.

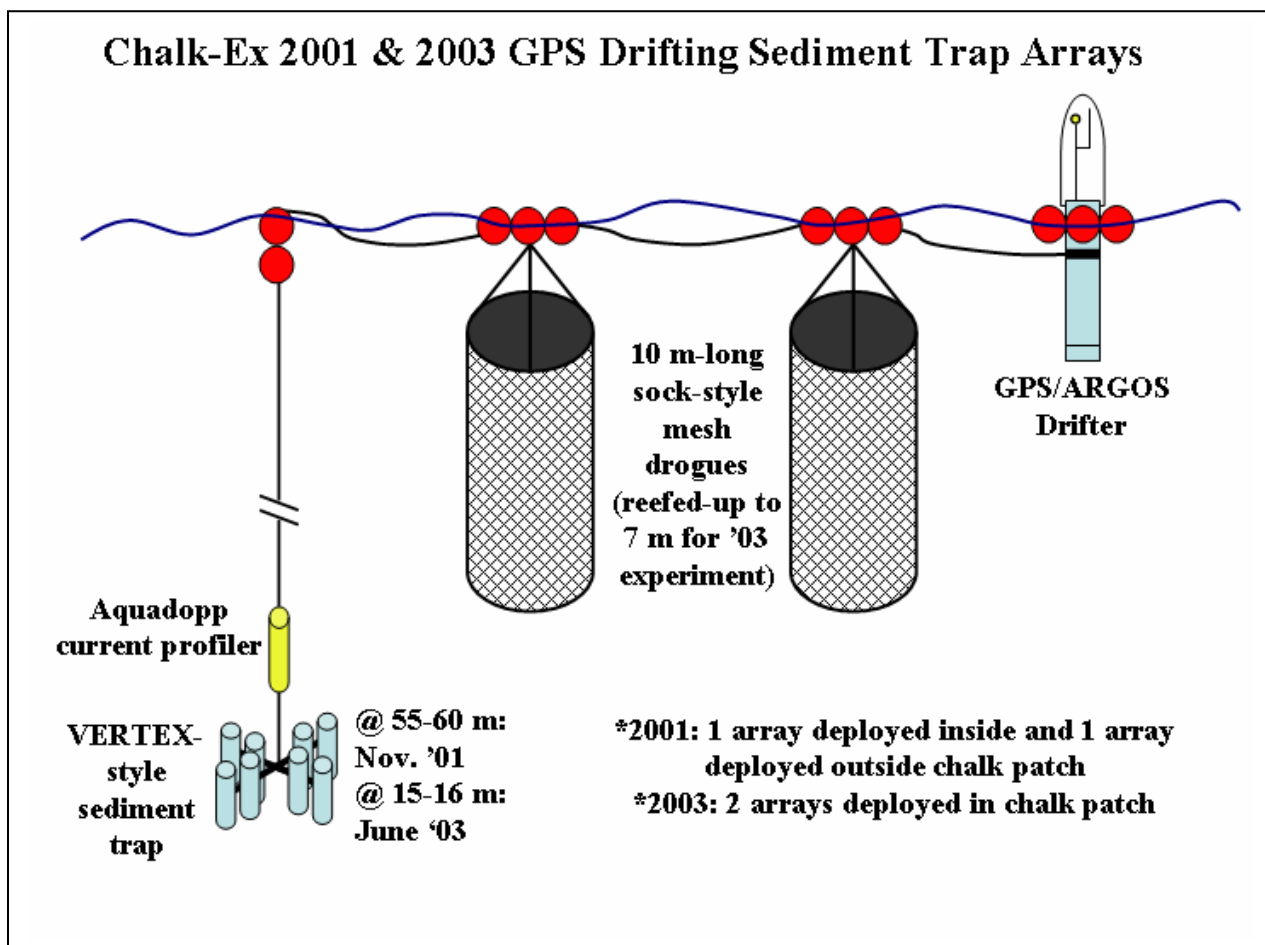


Fig. 1- Diagrams showing drifting sediment trap arrays, sock-style drogues and GPS/ARGOS drifters that were used in Chalk-ex experiments.

RESULTS

The optical results from the Chalk-Ex experiments demonstrated that the most significant factor affecting chalk distribution was horizontal physical dispersion. Sinking, zooplankton grazing and aggregation were also quantified, albeit the chalk loss rates due to these processes were secondary to losses due to physical dispersion. For more information on the physical processes, see previous reports by Dr. A. Pleuddemann (Woods Hole Oceanographic Inst.; N000140110141). For more information on the aggregation and grazing processes involved in dispersing the chalk, see previous reports of Dr. H. Dam and Dr. G. McManus (Univ. Connecticut; N000140110016). Effects of physical

processes can best be seen when viewing the horizontal layer maps of the chalk. For example, maps of the chalk concentration were calculated using the Lagrangian-corrected data, integrated through 4 layers, 0-3m, 3-12m, 12-20m and 20-30m. The results showed the well-focused patch centered between 0 and 12m during the first survey (2h post-deployment). By the second survey (9h post-deployment), the patch was located in approximately the same location horizontally, but centered in the 12-20m layer. Moreover, while the amount of chalk accounted in each survey was about the same, it can be seen that the patch was considerably more aerally dispersed in the second survey (note, the integrated chalk concentration was calculated by subtracting a “pre-chalk” blank, estimated from a complete Scanfish survey immediately prior to chalk deployment). (Fig. 2).

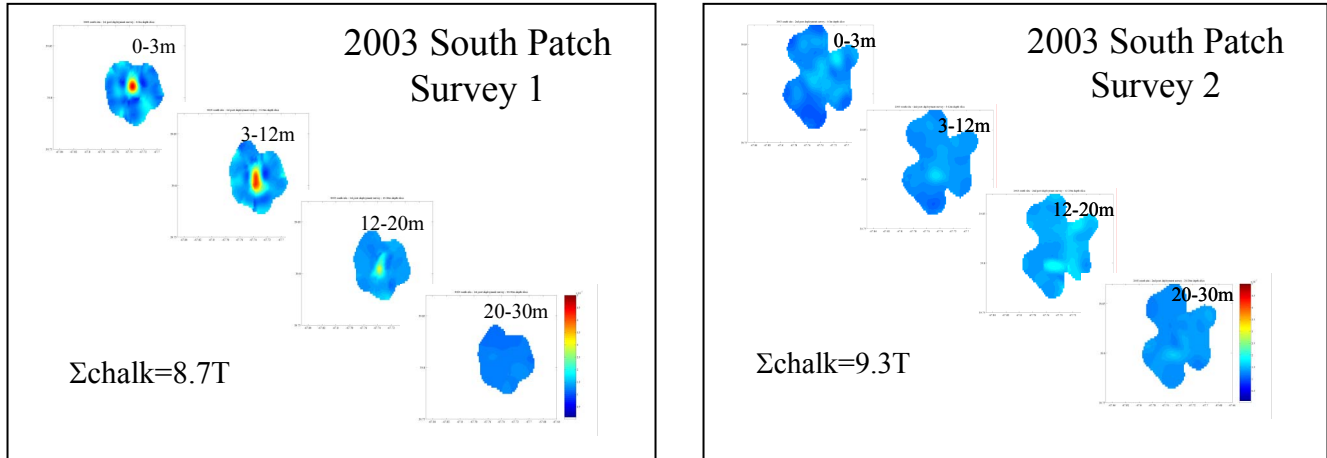


Figure 2- Aerial maps of chalk concentration (longitude on X axis and latitude on Y axis) for each of 4 depth layers in the 2003 South patch. Contours of backscattering are shown in color (color bar shown in each panel where red and blue extremes represent high and low backscattering respectively) Each layer is plotted in the same, Lagrangian-corrected coordinate space. Results are contoured using geophysical Kriging analyses. Total mass of chalk estimated from each survey is given in the lower left corner of each panel.

An unexpected observation was the production of a thin layer of chalk, 1-2m thick, at a depth of 15-20m. This was most easily seen when superimposing the Scanfish sections of backscattering with density (Fig. 3). During the first survey, the patch had already crossed 0.1 sigma-theta contours, penetrating as deep as 15m (but mostly centered at 5-10m). There was already evidence of sheering at the base of the patch after 2h deployment. By 9h post-deployment, however, the chalk was focused in a thin layer, spread over length scales of over 10km. We believe that the chalk was focused into this thin layer via physical shear dispersion.

The other observation worthy of note was that the descent rate of the chalk between the different layers was faster than could be accounted for by simple sinking of well dispersed particles (which, in the laboratory was determined to be $<1\text{m/d}$). Examinations of the chalk distribution on TS plots also showed that the chalk “jumped” across isopycnals between surveys (Fig. 3B). One explanation for this is that the thick chalk suspension injected into the patch actually increased the effective density of the composite fluid/suspension mixture causing it to sink more rapidly. Such an observation has support from other observations of seawater composition, POC content and density (Millero 2000).

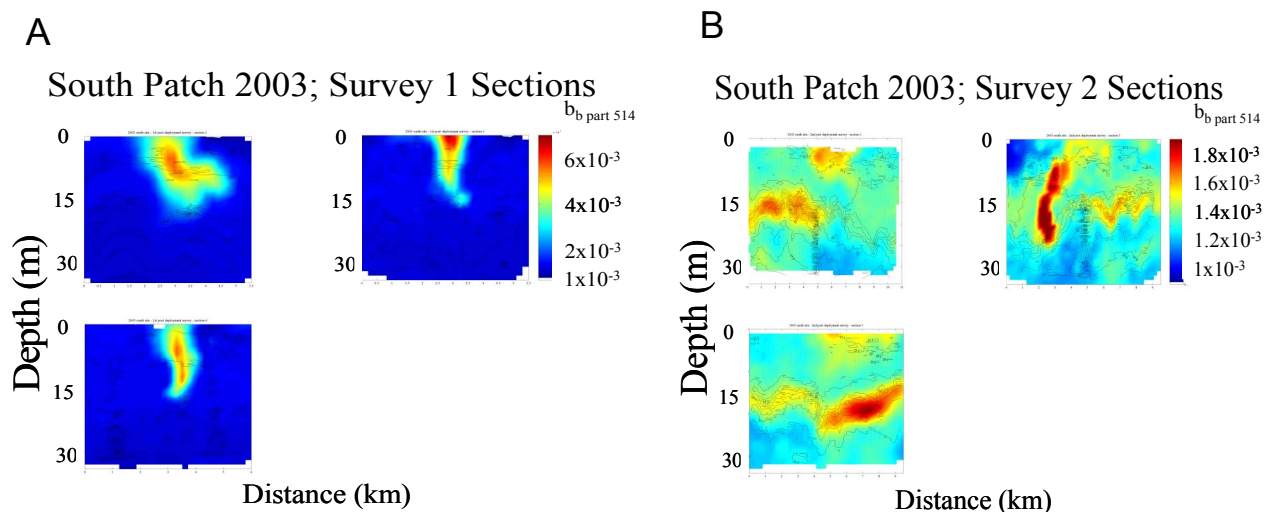


Figure 3-Vertical sections of backscattering from the south patch, 2003. A) Three panels show different sections from the first Scanfish survey (2h after chalk deployment). They show the vertical penetration of the chalk into the surface mixed layer. B) Three vertical sections from the second survey (9h post deployment). Color contours represent backscattering with red and blue areas representing highest and lowest backscattering respectively. Isopleths of density are superimposed in black. Note Chalk thin layer observed across entire patch in survey 2 (>10km) which is highly coherent with density structure.

Below, we summarize the sediment trap results for the two cruises. The November '01 chalk patch at the north site had strong winds and the chalk was mixed into the top 70m almost as fast as it was added to the surface water. While the increase in backscattering was measurable, it rapidly decreased to background levels and was impossible to locate with either the Scan-Fish or with surface sampling within several hours of deployment. High winds and sea-state resulted in the loss of the in-patch trap at the north site. At the south site, there was more stratification and the chalk was detectable for several days. The drifter that best followed the patch was the sediment trap drifter, drogued to the top 10m. Dispersion of the chalk between the hydrographic drifter, Lagrangian drifters, and sediment trap drifters illustrated the mixed layer shear. During the first 40 hours after chalk injection, the upper 40 m of the water column restratified. We were able to account for all the chalk within the first 6h after the patch was dispersed, but the measurable chalk decreased exponentially over time thereafter. Optical patch definition, using light scattering results and above-water radiance measurements, was in good agreement. Based on stable isotope and microscopic analyses of the collected drifter trap material, no appreciable amount of the chalk settled into the sediment traps during November '01 at the south site. Stable isotope analyses ($\delta^{18}\text{O}$) of the trapped detrital material, from which planktonic forams and pteropods were removed, revealed a slightly depleted but relatively strong, planktonic calcite signature, not the highly depleted value typical of Cretaceous chalks (Table 2).

Table 1: Chalk-Ex sediment trap geochemical data summary, including total mass flux, % CaCO₃, CaCO₃ flux, %POC and POC flux.

	<u>2001 So. Site</u> <u>In-patch traps</u>	<u>2001 So. Site</u> <u>Out patch traps</u>	<u>2003 So. Site</u>	<u>2003 No. Site</u>
Total Mass Flux (g m ⁻² d ⁻¹)	1.4 ±0.1 (n = 5)	1.8 ±0.1 (n = 6)	1.0 ±0.01 (n = 5)	4.1 ±1.1 (n = 7)
% CaCO ₃	36.3 ±0.6 (n = 2)	27.3 ±2.2 (n = 2)	3.1 ±3.1 (n = 3)	0.2 ±0.2 (n = 8)
CaCO ₃ Flux (mg m ⁻² d ⁻¹)	50.0 ±0.1	50.5 ±0.1	2.8 ±2.8	17.9 ±8.1
% POC	25.9 (n = 2)	26.6 (n = 2)	46.9 ±2.8 (n = 3)	48.7 ±2.1 (n = 8)
POC Flux (g m ⁻² d ⁻¹)	0.4	0.5	2.2 ±1.7	2.0 ±0.6

These results, coupled with the lack of chalk-containing fecal pellets and/or chalk-containing organic aggregates in the traps, indicated that biogenic and/or physical aggregation of chalk particles were not important mechanisms contributing to the fate of the chalk particles during the November '01 experiment. Supporting this finding was the observation by Dam and McManus of minimal chalk grazing by macrozooplankton and measurable chalk grazing by microzooplankton resulting in very small fecal pellets with extremely low/negligible sinking rates. Additionally, we collected fecal pellets from net-haul copepods in 2001 that were incubated in chalk patch water. The pellets were analyzed for $\delta^{18}\text{O}$ in order to see if we indeed could obtain a Cretaceous chalk isotope signature from biogenic particle aggregates which we knew were produced by suspension feeders that were effectively forced-fed chalk-water. The $\delta^{18}\text{O}$ signature of the copepod fecal pellets was very close to that of the Cretaceous chalk standard (-4.02 for the former and -4.71 for the latter). For comparison, Gulf of Maine planktonic forams have a value of -0.43 and Gulf of Maine coccoliths show a value of +0.65 (Paull and Balch 1994). This experiment and the results allowed us to say with certainty that we should expect to see a Cretaceous chalk $\delta^{18}\text{O}$ value in sinking particulate material collected under the patch if, in fact, biogenic aggregation of the chalk particles occurs and if such particulates have an appreciable sinking rate so that they are collected in the traps. The results also confirmed our above conclusion that such aggregation did not occur or did not represent an important mechanism for the removal of the chalk from the patch in November 2001.

During the June'03 deployment, intense stratification restricted the chalk in the top 15m at both sites such that the chalk signal was detectable for at least 48h. The chalk quickly became associated with frontal boundaries, as evident during the Scanfish surveys. There were significant populations of zooplankton in Jordan Basin observed during net hauls and thus we expected significant chalk clearing by zooplankton at that site. The drifter trap arrays, along with the two Lagrangian drifters drogued to different depths, provided a fairly accurate idea of the location of the chalk patches throughout the experiments. Microscopic and isotopic evidence from the traps deployed in the particle-rich, productive north site in the Gulf of Maine documented chalk incorporation into zooplankton fecal

pellets as well as the passive physical scavenging of chalk particles onto sinking, flocculent/algal-rich detritus. No naturally-occurring planktonic carbonate particles were collected in the north site drifter traps. Much lower particle fluxes were measured with the traps at the more oligotrophic south site where the carbonate components consisted of a mix of naturally occurring planktonic calcite and aragonite in the form of abundant coccoliths and coccospheres, and occasional forams, pteropods and larval gastropods.

The $\delta^{18}\text{O}$ signature of the 2003 north site trap material showed a clear, highly depleted Cretaceous chalk signature (Table 2). The sinking material collected below the mixed layer at the 2003 south site displayed a slightly positive $\delta^{18}\text{O}$ value that most likely represented a mixture of carbonates of primarily coccoliths (slightly positive values) and possibly a small contribution by highly depleted $\delta^{18}\text{O}$ Cretaceous chalk (Table 2).

We have contacted Deep Sea Research II about a special issue on the Chalk-Ex experiments and are writing papers for it. The layout of this issue will be: 1) executive summary, 2) evolution of upper-ocean physical structure during ChalkEx, 3) evolution of the optical signals during Chalk-Ex, 4) trophodynamics of chalk, 5) aggregation phenomena during Chalk-Ex, 6) transport of optically reflective particles below the upper mixed layer via particle aggregation and sinking: drifter sediment trap results from Chalk-Ex, and 7) evidence of colloidal DOM removal by cretaceous chalk particles during Chalk-Ex I and II cruises.

IMPACT/APPLICATIONS

These experiments were designed to identify the major loss terms of optically-active particles. This indeed was accomplished. Such information is critical for understanding the evolution of the underwater optical field and prediction of underwater visibility on horizontal and vertical spatial scales of 1-10,000 m and 1-100m, respectively, and time scales of hours to several days. Observations of adsorption of chromophoric DOC onto chalk particles has ramifications to the fate of DOC, the largest organic pool in the sea. Overall, the data demonstrate how important physical mixing conditions are to the initiation and retention of a highly reflective coccolithophore bloom. The potential importance of microzooplankton (relative to macrozooplankton) to loss of the chalk was unexpected and has implications to calcite dissolution and turnover in the sea. The observation of potential changes in suspension density due to concentrated additions of chalk also has ramifications to density-dependent circulation in coastal embayments where sediment suspension could affect the bulk density of the water.

RELATED PROJECTS

Dr. H. Gordon (U. Miami) and W. Balch have collaborated in earlier chalk experiments as part of a NASA MODIS contract to derive a remote sensing algorithm for the determination of CaCO_3 from space. Downwelling radiance measurements from Chalk-Ex were used by H. Gordon (Univ. Miami) for inverse modeling of inherent optical properties (presented at Ocean Optics, October 2004).

Table 2- Stable isotope results ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) from Chalk-ex 2001 and 2003 cruises plus standard deviation values for determinations. Standard isotope ratios for Cretaceous limestone, planktonic foraminifera, pteropods and coccoliths are provided for comparison.

	$\delta^{18}\text{O}$		$\delta^{13}\text{C}$	
<u>Standards</u>				
Cretaceous limestone chalk (w/ & w/o formalin)	-4.71	(±0.09)	2.00	(±0.05)
Planktonic Forams (Chalk-Ex 2001 So. Site traps)	-0.04	(±0.01)	0.49	(±0.04)
Pteropods (from Chalk-Ex 2001 So. Site traps)	1.00		1.14	
Coccoliths from GoM (Balch and Paull 1994)	0.65	(±1.10)	NA	
<u>Particulate samples</u>				
2001 So Site In-patch trap:	-0.28		0.43	
CaCO ₃ tests removed-detritus only	-0.87		0.16	
2001 So. Site Out-patch trap:	-0.57		-0.10	
CaCO ₃ tests removed, detritus only				
2001 So. Site Copepod fecal pellets	-4.37		1.08	
2003 So. Site (CaCO ₃ tests removed)	0.42		0.1	
2003 No. Site (CaCO ₃ tests removed)	-4.05		-2.46	

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